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Electrically tunable behaviors of lead barium zirconate titanate films

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Abstract

Tunable $(Pb_{0.5}Ba_{0.5})(Zr_{1-x}Ti_x)O_3$ (PBZT) films were grown on Pt/Ti/SiO_2/Si substrates using chemical solution deposition method. PBZT films contained bimodal distribution of grains and pores. The size of large grains, the amount of small grains, and the porosity all increased with the content of titanium oxide. The microstructural characteristics of PBZT films influenced dielectric properties. Increasing the content of TiO_2 in PBZT films increased dielectric constant, tunability, and figure of merit (FOM), while it kept loss tangent relatively unchanged. The composition ($x=0.2$) locating near the paraelectric–ferroelectric boundary exhibited optimal dielectric tunability and FOM. The tunability and FOM were improved remarkably from 12% and 6 to 34% and 26, respectively, when 20% of titanium oxide was added to PBZ films.

Keywords: Lead barium zirconate titanate films; Electrically tunable behavior; Chemical solution deposition

1. Introduction

The development of tunable dielectric materials for microwave device applications [1,2] has attracted considerable interest recently. The improvement in the performance of tunable dielectric materials is very beneficial to the design of microwave components such as voltage controlled oscillators, varactors, delay lines, and phase shifters [3,4]. Barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$) thin film has been considered to be the foremost candidate for such tunable components at room temperature. One of the major challenges encountered for realizing the integration of BST thin films into electrically tunable devices is simultaneous minimization of the dielectric loss and maximization of dielectric tunability. Attempts in improving dielectric properties of BST thin films have been focused on texturing of the films [5], improvement of the dielectric–electrode interface, control of film stress [6–9], addition of dopants [10–12], and modification of microstructures [13,14]. Almost no attempt has successfully improved the dielectric tunability and dielectric loss simultaneously. Recently, materials in the lead barium zirconate ($Pb_{1-x}Ba_xZrO_3$, PBZ) system have been reported to possess properties comparable to BST [15].

PBZ is a series of materials with perovskite structure [16–18], exhibiting antiferroelectric as $x=0$ to 0.2, ferroelectric as $x=0.2$ to 0.4, and paraelectric as $x=0.4$ to 1. The perovskite structure of PBZ is tetragonal in the anti-ferroelectric region, rhombohedral in the ferroelectric region, and cubic in the paraelectric region. Although the ferroelectric and anti-ferroelectric phases which possess high dielectric loss are not suitable for electrically tunable applications, the paraelectric phase of the PBZ ($x=0.4$ to 1) materials is a potential candidate like its BST counterpart. The paraelectric phase of the PBZ were recently reported to possess good tunable dielectric behavior [15]. It was found that the composition region which exhibited best dielectric tunable behavior was close to the paraelectric–ferroelectric phase boundary, $x=0.4$. Replacement of Ti for Zr generally increases dielectric loss and tunability of perovskite materials. It is possible that an optimal addition of titanium oxide exists that produces maximal *figure of merit (FOM)*. In this paper, we report the effect of added titanium oxide on dielectric tunable characteristics of $(Pb_{0.5}Ba_{0.5})(Zr_{1-x}Ti_x)O_3$*(PBZT)* films. The base composition of PBZ chosen was $(Pb_{0.5},Ba_{0.5})ZrO_3$, locating away from the ferroelectric–paraelectric boundary of the PBZ $(Pb_{0.65},Ba_{0.35})ZrO_3$ so that more TiO_2 could be added in

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the paraelectric field of the PBZT system to clearly clarify the TiO_2 effect.

2. Experimental procedures

The PBZT thin films were prepared by chemical solution deposition process. The precursor solution was synthesized from lead acetate trihydrate (Riedel-de Ha¸n), barium acetate (Riedel-de Ha¸n), zirconium acetylacetonate (Fluka), and titanium di-isopropoxide bis 2,4-pentanedionate (Fluka). Lead acetate trihydrate and barium acetate were dissolved in acetic acid and mixed at 110 °C for 6 h to remove the crystallized water. The concentration of the solution was 0.3 mol/kg and the prepared volume of the solution was 100 ml. After the temperature was lowered to 70 °C, zirconium acetylacetonate was added into the solution and mixed for 3 h. Next, titanium di-isopropoxide bis 2,4-pentanedionate was added at 70 °C and mixed for 3 h. Finally, the concentration of the precursor solution was adjusted to 0.2 mol/kg by adding acetic acid and then cooled to room temperature. The nominal composition of the solution is described as $(Pb_{0.5}Ba_{0.5})(Zr_{1-x}Ti_x)O_3$ ($x=0$, 0.1 and 0.2, expressed as T0, T1, T2, respectively) with 5 mol% excess Pb for lead loss compensation. To fabricate PBZT thin films, the precursor solution was spin-coated on $Pt/Ti/SiO_2/Si$ substrates under 2500 rpm for 30 s, followed by baking at 150 °C for 5 min and then 350 °C for 10 min. The spin coating process was generally repeated 4 times. The films were then heated at 650–750 °C for 20 min in O_2 atmosphere. The thickness of the heat-treated PBZT films was approximately 280 nm.

Measurement of electric properties was conducted in the form of metal–insulator–metal capacitor cell. Pt electrodes having diameter of 100 μm were deposited on the PBZT films by *DC* sputtering. X-ray diffraction (XRD) patterns were carried out using Cu Kα radiation source (Rigaku-D/MAX). The surface morphology was analyzed by field emission scanning electron microscope (SEM) (JSE 6500F). Polarization–electric field (P–E) curves of the PBZT films were determined by RT66A (Radiant Technology). Capacitance–voltage measurements were carried out at 1 MHz by using HP 4284 analyzer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the PBZT thin films annealed at 650 °C, 700 °C, and 750 °C for the three compositions (T0, T1, and T2). All films exhibit pure perovskite structure without secondary phases. The peak intensity of perovskite phase increases with annealing temperatures for each composition, indicating that crystalline quality of perovskite phase improves with temperature. In contrast, substitution of Ti for Zr does not affect the peak intensities of the films. Thus, the content of titanium oxide does not have significant effect on the formation of perovskite phase nor on the crystal quality of the films. The diffraction peaks shift to higher angles, demonstrating that lattice constants decrease with the content of titanium oxide.

Fig. 2 displays the microstructures of three films annealed at 750 °C. PBZT films contain bimodal distribution of grains. The large grains are 50–100 nm and small ones are 3–5 nm. The

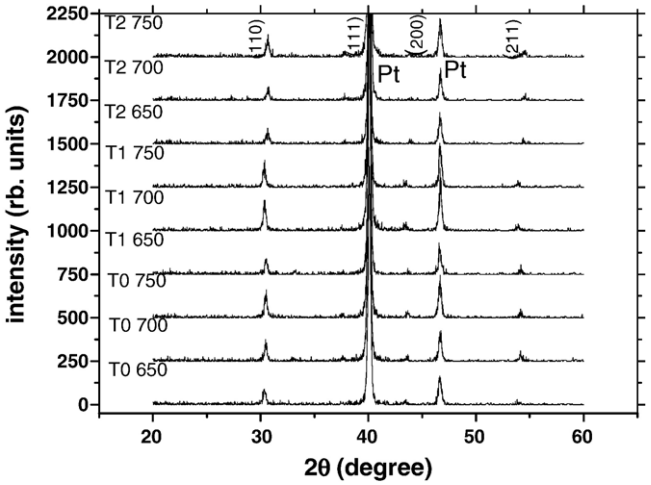

Fig. 1. XRD patterns of T0, T1, and T2 films annealed at 650 °C, 700 °C, and 750 °C.

small grains concentrate among large grains. The size of large grains and the amount of small grains increase with increasing content of titanium oxide. Moreover, the porosity of PBZT films also increases with the amount of titanium oxide. PBZT films annealed at 650 and 700 °C possess similar microstructural characteristics, except that the grain size, the porosity, and the degree of bimodal distribution decrease with decreasing annealing temperature within the 650–750 °C range. The observed microstructural features demonstrate that strong competition occurs between grain growth and densification. The results can be interpreted as follows. The rate of grain growth increases much faster than that of densification as the content of titanium oxide increases. Pores are left behind when grain growth proceeds much faster than densification. It results in larger grains and higher porosities. The small grains are loosely-packed perovskites that cannot be densified in time. The amount of small grains was about 20 vol.% in T2 films, but no second phases were detected by XRD. Therefore, the small grains should be perovskite too. To clarify the argument, *energy-dispersive X-ray spectroscopy* was employed to analyze the elements of both large and small grains. The results showed that they contained same elements and compositions. Similar microstructures were reported previously [15].

T0 and T1 films annealed at 650–750 °C exhibit linear P–E lines, indicating that they are paraelectric. For T2 films annealed at 650 °C, the P–E behavior is similar to that of T0 and T1 films. But T2 films annealed at 700 and 750 °C exhibit slender hysteresis loops with small remnant polarizations of about 0.2 and 1 $\mu C/cm^2$ (as shown in Fig. 3), respectively. The results suggest that the T2 composition is around the paraelectric–ferroelectric phase boundary so that variation in annealing conditions provokes it to change from paraelectric to ferroelectric. Generally, the polarizations of materials decrease with their porosities. The polarizations of T2 films are larger than those of T0 and T1 films, although T2 films possess higher porosities. It demonstrates that T2 films should have much higher polarizable capability than T0 and T1 films to offset the influence of the increased porosity with the increasing content of titanium oxide.

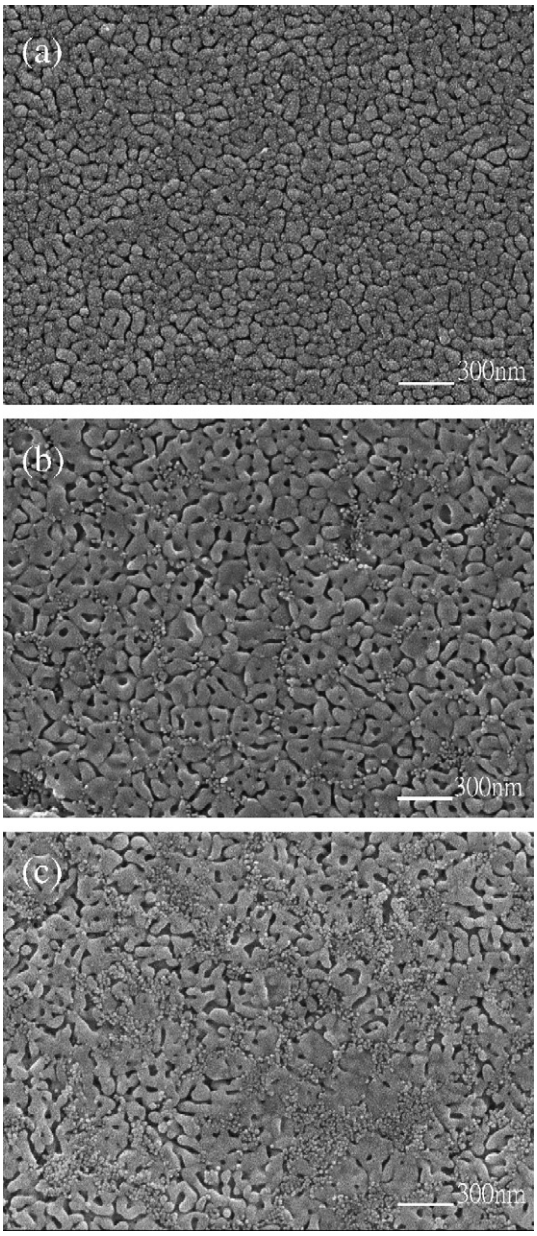

Fig. 2. SEM images of (a) T0, (b) T1, and (c) T2 thin films annealed at 750 °C.

Fig. 4 expresses the bias-field dependence of dielectric constant and loss tangent of the T2 films measured at 1 MHz. The dielectric constant and the variation of dielectric constant with bias field increase with annealing temperatures. All three films have the same trend, but the obtained values differ greatly. The dielectric constant and the variation of dielectric constant with bias field of T2 films are much larger than those of T0 and T1 films. Fig. 5 plots dielectric constant and loss tangent of PBZT films measured at zero-bias. The dielectric constants increase with annealing temperatures and with the content of titanium oxide. The increase of dielectric constant is not proportional to the content of titanium oxide. The dielectric constants increases from 20–40 of T0 films to 60–90 of T2 films, and the major part of the increase occurs from T1 to T2. The loss tangent of T0 and T1 films increases with temperature first and then decreases. This is due to competitions between the

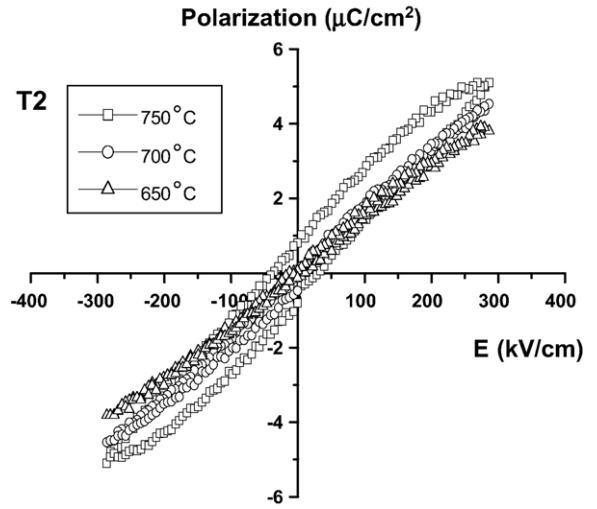

Fig. 3. P–E hysteresis loops of T2 films annealed at 650 °C, 700 °C, and 750 °C.

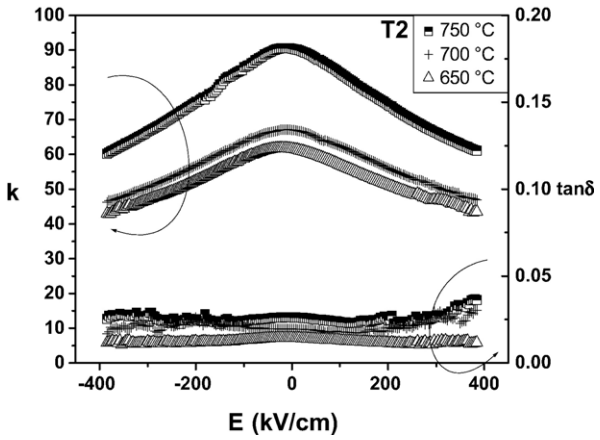

Fig. 4. DC bias-field dependent dielectric constant and loss tangent of T2 thin films.

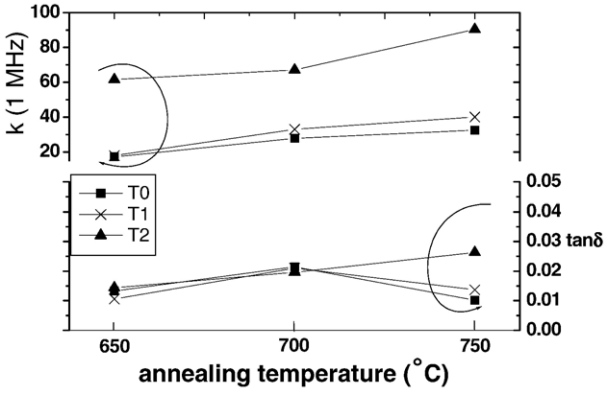

Fig. 5. Dielectric constant and loss tangent of films measured at zero-bias.

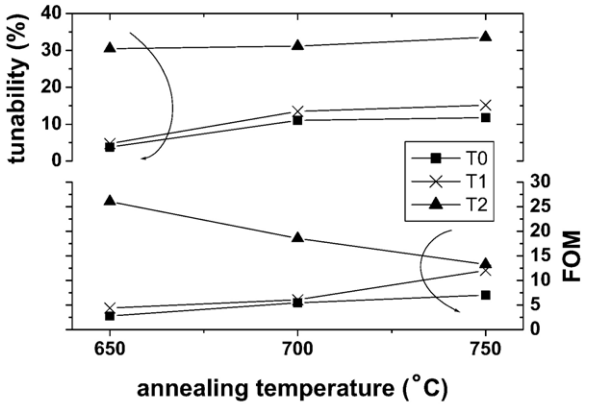

Fig. 6. Tunability and FOM of T0, T1, T2 thin films annealed at 650 °C, 700 °C, and 750 °C.

influence of grain size effect and porosity effect. Loss tangent generally increases with grain size and decreases with porosity. All three films have very similar loss tangent except for the T2 film annealed at 750 °C. The loss tangent of the T2 film is not reduced with annealing temperature like T0 and T1 films, because it exhibits weak ferroelectric behavior which results in the increase of loss tangent with temperature.

The dielectric tunability was calculated by the formula:

$$\text{tunability} = \frac{k_0 - k_e}{k_0} \times 100\%,$$

where k_0 and k_e represent the dielectric constant value at zero and the maximum applied electric field, respectively. Fig. 6 displays the variation of tunability of PBZT films with annealing temperature. The dielectric tunability of the PBZT films increases with the content of titanium oxide. They are 12%, 15% and 34% for T0, T1, and T2 films annealed at 750 °C, respectively. Rapid increase of tunability takes place from T1 to T2. According to one of the previous reports [19], the tunability of dielectric films always increases with the dielectric constants of films. The results obtained in this study also confirm the fact. In addition to the observed fact, the internal stress in the films [8,9] and grain size [14] may play an important role on the tunability of films. The T2 film locates near the paraelectric–ferroelectric phase boundary. Paraelectric–ferroelectric transformation tends to relax internal stress in the film, which is advantageous to raise tunability of T2 films. The T2 film which possesses larger grain size than the other two films is also beneficial to the increase of tunability. Based on the observation, it is believed that the effect of internal stress is more important than that of grain size in the investigated films, because grain size stays relatively the same between T1 and T2 films.

In electrically tunable applications, the figure of merit (FOM) is usually used to evaluate the quality of ferroelectric films. The FOM is defined as:

$$\text{FOM} = \frac{\text{tunability}}{\tan\delta}$$

Fig. 6 also exhibits the FOM of PBZT films as a function of annealing temperature. The FOM of the T0 and T1 films increases with annealing temperature. This is because their tunabilities increase with temperature, while loss tangents are relatively unchanged. In contrast, the FOM of T2 films decreases with temperature because the loss tangent of the films increases with temperature significantly. The improvement of FOM from T0 to T1 is slight, increasing from 3–6 to 4–12 only. However, the FOM of the T2 film annealed at 650 °C is improved significantly with a value of 26, which is about 4 times of the PBZ films without titanium oxide added. The substitution of titanium oxide for zirconium oxide improves the FOM of PBZ films markedly, especially at the T2 composition which is thought to be around the paraelectric–ferroelectric phase boundary. At compositions near the phase boundary, the optimal annealing temperature tends to shift to lower temperature, which is advantageous for device processing.

4. Conclusion

In sum, tunable PBZT films were grown on Pt/Ti/SiO_2/Si substrates using chemical solution deposition method. The addition of titanium oxide affected microstructural development of PBZT films greatly, which influenced their dielectric properties. Substitution of titanium oxide for zirconium oxide in PBZT films increased dielectric constant and tunability, while it kept loss tangent relatively unchanged. The composition (x=0.2) locating near the paraelectric–ferroelectric boundary exhibited optimal dielectric tunability and FOM. The tunability and FOM were improved remarkably from 12% and 6 to 34% and 26, respectively, when 20% of titanium oxide was added to PBZ films.

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References

[1] B.H. Park, E.J. Peterson, Q.X. Jia, J. Lee, X. Zeng, W. Si, X.X. Xi, Appl. Phys. Lett. 78 (2001) 533.
[2] K.R. Carroll, J.M. Pond, D.B. Chrisey, J.S. Horwitz, R.E. Leutchner, Appl. Phys. Lett. 62 (1993) 1845.
[3] S.G. Lu, X.H. Zhu, c.L. Mak, K.H. Wong, H.L. Chan, C.L. Choy, Appl. Phys. Lett. 82 (2003) 2877.
[4] M.W. Cole, W.D. Nothwang, C. Hubbard, E. Ngo, M. Ervin, J. Appl. Phys. 93 (2003) 9218.
[5] Y.A. Jeon, E.S. Choi, T.S. Seo, S.G. Yoon, Appl. Phys. Lett. 79 (2001) 1012.
[6] T.R. Taylor, P. Hansen, B. Acikel, N. Pervez, R.A. York, S.K. Streiffer, J.S. Speck, Appl. Phys. Lett. 80 (2002) 1978.
[7] T.M. Shaw, Z. Suo, M. Huang, E. Liniger, R.B. Laibowitz, J.D. Baniecki, Appl. Phys. Lett. 75 (1999) 2129.
[8] Z.-G. Ban, S.P. Alpay, J. Appl. Phys. 93 (2003) 504.
[9] A. Sharma, Z.-G. Ban, S.P. Alpay, J.V. Mantese, Appl. Phys. Lett. 85 (2004) 985.
[10] M.W. Cole, P.C. Joshi, M.H. Ervin, J. Appl. Phys. 89 (2001) 6336.
[11] K.B. Chong, L.B. Kong, L. Chen, L. An, C.Y. Tan, C.K. Ong, T. Osipowicz, J. Appl. Phys. 95 (2004) 1416.

[12] Y.A. Jeon, T.S. Seo, S.G. Yoon, Jpn. J. Appl. Phys. 40 (2001) 6496.
[13] D.M. Bubb, J.S. Horwitz, S.B. Qadri, S.W. Kirchoefer, C. Hubert, J. Levy, Appl. Phys., A 79 (2004) 99.
[14] D.M. Potrepka, S. Hirch, M.W. Cole, W.D. Nothwang, S. Zhong, S.P. Alpay, J. Appl. Phys. 99 (2006) 014108.
[15] M.H. Wu, J.M. Wu, Appl. Phys. Lett. 86 (2005) 022909.
[16] B.P. Pokharel, D. Pandey, J. Appl. Phys. 86 (1999) 3327.
[17] B.G. Shirane, S. Hoshino, Acta Crystallogr. 7 (1954) 203.
[18] B.P. Pokharel, D. Pandey, J. Appl. Phys. 88 (2000) 5364.
[19] A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh, N. Setter, J. Electroceram. 11 (2003) 5.